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ABSTRACT

EMF measurements were performed at 25° and 35°C on the general cell M(s)/MCl [solution in $AlCl_3$ (1m) in PC]/TlCl(s)/Tl(Hg), where M represents Li, Na, K, Rb, and Cs. The standard electrode potentials of the alkali metals in $AlCl_3$ (1m) — PC solution evaluated by extrapolation to infinite dilution follow the order: Cs $<$ Rb $<$ K $<$ Li $<$ Na which is different than the order in water. Activity coefficients of the alkali metal chlorides were calculated for a wide range of molalities. The partial molal Gibbs free energies, entropies, and enthalpies of the cell reactions have been evaluated and compared to those in other solvents.

The feasibility of the deposition of all the alkali metals from their chlorides in $AlCl_3$-propylene carbonate solution has been demonstrated (1). Lithium, sodium, potassium, rubidium, and cesium were deposited at ambient temperature showing stable and reversible behavior. The alkali metal chlorides are practically insoluble in PC, however in the presence of $AlCl_3$ a complex is formed between the chloride and $AlCl_3$ according to the reaction

$$MCl + AlCl_3 = M^+ + AlCl_4^-$$

This reaction proceeds for all the alkali metals and is the only combination that gives high solubility and conductivity for all the alkali metals. The electrodeposition of the alkali metals from their chloride solutions in $AlCl_3$-PC is proposed as a new process for the electrodeposition and refining of the alkali metals at ambient temperature (2). In order to characterize such a process, thermodynamic, kinetic, and transport data are needed. With this goal in mind, emf measurements of the alkali metals in their chloride solutions in $AlCl_3$(1m)-PC were performed on the cell

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Key words: alkali metals, propylene carbonate, aluminum chloride, standard potentials.

$M(s)/MCl(m), AlCl_3(1m)$ in $PC/TlCl(s)/Tl(Hg)$

The measurements were performed in order to establish a scale of standard electrode potentials in $AlCl_3(1m)$-PC solution, and to obtain activity coefficients data; both are needed for the design of an electrorefining cell, and for the prediction of the separation and purification of the alkali metals in such a cell (2). In addition, kinetic (3), conductance, and specific volume measurements (4) are reported elsewhere.

The thermodynamics of some of the alkali metals in various solutions in PC were investigated by Salomon (5-7) using the emf method. The thermodynamics of LiCl and LiBr (5), NaI (6), LiI and KI (7), were measured using the cell-type

M/MX in $PC/TlX(s)/Tl(Hg)$

where M represents Li, Na, and K, and X represents Cl^-, Br^-, and I^-. In the case of the potassium system, potassium amalgam replaced the metallic potassium, and the data were corrected for the free energy of formation of the amalgam. The standard potentials were obtained by extrapolation to infinite dilution following the Guggenheim equation (8). The thermodynamics of single ion solvation in PC and water is summarized by Salomon (9).

The extensive work of Salomon did not include rubidium and cesium and in addition, iodide was the only common anion which shows high solubility for Li, Na, and K. With the exception of lithium, the chlorides of the alkali metals are highly insoluble in pure PC. In the present work, emf measurements were performed for all the alkali metals, and the fact that the same common anion was used enabled the establishment of a scale of standard potentials for the alkali metals series.

Experimental

Solvent purification.—Propylene carbonate (Jefferson Chemical Company, Houston, Texas) was distilled at 0.5 mm Hg in a commercially available distillation column (Semi-CAL Series 3650, Podbielniak, Franklin Park, Illinois) packed with stainless steel helices. The reflux ratio was 60 to 100 and the head temperature 65°C. The first 10% and last 25% of the solvent were discarded. Argon gas was bubbled through the solvent during distillation. The collection vessel was not detached from the column; the solvent was discharged directly into the dispensing vessel. The transfer was done under an argon atmosphere. The dispensing vessel was evacuated on the vacuum line to approximately 50μ Hg, closed tightly and transferred into the glove box.

The "as received" solvent contains a few tenths of a per cent of the following impurities: water, propylene glycol, propion aldehyde, propylene oxide (10). Gas chromatographic analysis of the product performed in this laboratory showed the water content to be always below 50 ppm. The presence of a second impurity at a very low concentration was identified as propylene oxide; its concentration was estimated below 1 ppm (1). Molecular sieves (Linde 4A) were ineffective in removing propylene oxide from PC.

The glove box (Lawrence Livermore Laboratory design) was maintained under dry and oxygen-free argon (1). The water content of the inlet argon stream was measured by a moisture monitor (Consolidated Electrodynamics Corporation, Model 26-303 ME) and was always below 1 ppm.

Electrolytic solutions.—All solutions of the alkali metal chlorides in $AlCl_3(1m)$-PC were prepared by weighing the salts and the solvent inside the glove box. The 1.0 molal (m) solutions of $AlCl_3$ in PC were made by adding the salt very slowly to the solvent, since the heat of solution is very high. The $AlCl_3$ in PC solutions were prepared inside the box under argon and were cooled with chloroform-carbon tetrachloride-dry ice bath mixture. Careless addition of $AlCl_3$ to PC resulted in a brown solution; this occurred particularly when the salt was not a fine powder, but rather in small granules, which upon addition to PC resulted in local heating and darkening of the solution.

The alkali metal chlorides were dried inside a vacuum oven (Hotpack, Philadelphia) at 200°C and approximately 50μ Hg for at least 24 hr. The amounts needed for the specific molalities were calculated each time from the weights of the solvent. Stirring for a few hours was required in order to achieve complete dissolution of the alkali metal chlorides. The final solutions were treated with molecular sieves (Linde 4A) in order to remove traces of water introduced by the salts. The molecular sieves were treated before use by heating (300°C), high vacuum, and several flashes with argon. This procedure was found effective in further removing traces of water and therefore increased the stability of the alkali metals during the potential measurements.

Reference electrode.—Earlier investigations in this laboratory revealed the excellent nature of thallium amalgam-thallous halide electrodes in PC (11) and DMSO (12, 13). Thallous chloride was found to be only slightly soluble in PC and does not dissolve in excess of chloride. This reference electrode has been applied to the cell $Li/LiX(DMSO)/TlX(s)/Tl(Hg)$ in order to determine the standard potential of the cell and the activity coefficients of LiX in DMSO. Salomon (5-7) used this reference electrode to measure standard potentials and activity coefficients of alkali metal halides in PC. The Tl(Hg) solidus TlCl electrode was found to be stable and reversible in DMF (12).

The performance of Tl(Hg)/TlCl electrode in PC was reversible with good stability. The solubility product of TlCl in PC is $K_{sp} = 10^{-12.4}$ (11), extremely low even when compared with other aprotic solvents (*e.g.*, for DMSO $K_{sp} = 10^{-6.26}$) (14).

The thallium wire used for preparation of the amalgam was 99.999% pure (United Mineral and Chemical Corporation, New York). The oxide coating on the metal was removed by successive washing with oxygen-free distilled water under argon atmosphere. The shining Tl was transferred directly into the glove box without exposure to air. The resulting silvery white metal dissolved readily in mercury. The mercury used was triple distilled. The amalgam concentration was prepared by weight. The thallium amalgam was then placed inside the electrode cups containing about 5 ml of the amalgam, exposing around 1 cm^2 of shiny surface (see Fig. 1). The amalgam surface was then covered with a thin adherent layer of fine TlCl. The electrode was gently shaken in order to get a complete and uniform coverage of the surface.

The electrical connection to the amalgam was through a platinum lead which was connected to a tungsten wire. All the connections and leads were overlaid with uranium glass for a vacuum-tight seal. The platinum tip was immersed well beneath the surface of the amalgam to prevent creeping of the solvent between the amalgam and the glass.

Cell for potential measurements.—The cell used for potential measurements, shown in Fig. 1, was developed earlier by Smyrl (13, 15). In this six-compartment cell each compartment is connected to the central one by a narrow pipe. The cup electrode for the thallium amalgam-thallous chloride reference electrode is shown in Fig. 1. A detailed description of the cell is given by Smyrl and Tobias (15). The electrode holder for the solid alkali metals (Li, Na, K) is shown in Fig. 1. The alkali metal wire was attached to the platinum wire by a stainless steel connector. Alkali metal amalgam electrodes were prepared by pouring the amalgams into cup electrodes similar to those used for the reference electrodes.

Rubidium and cesium electrodes were prepared by heating the capsules in which these metals had been received, and the electrode's cups, and then pouring the

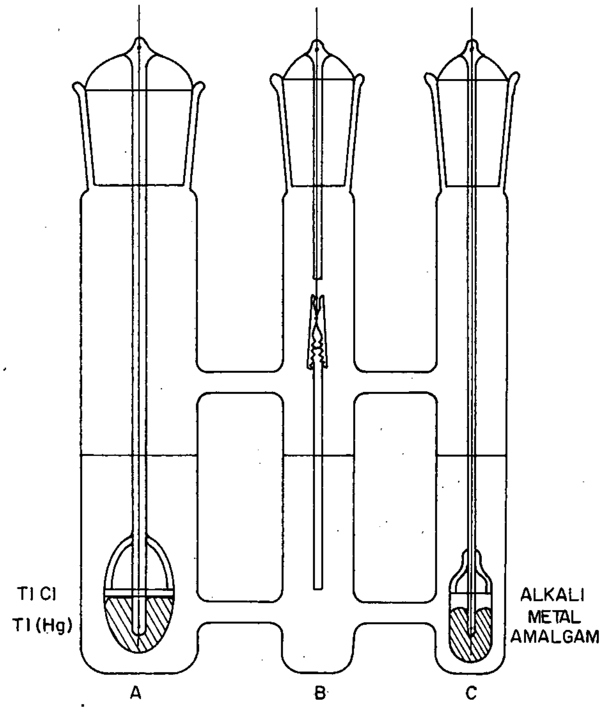

Fig. 1. Six-compartment cell for potential measurements (only three compartments are shown). A, Reference electrode; B, alkali metal electrode; C, alkali metal amalgam electrode.

liquid metals into the cups well above the platinum leads. Lithium was obtained as ⅛ in. wire and was rinsed with the pure solvent. Sodium and potassium obtained in the form of ribbons were extruded through a stainless steel extruder of 1.13 cm diameter, and then were washed with the pure solvent. All the alkali metal electrodes kept their shining surfaces during the measurements. Electrodes which turned gray or black after being immersed in the solution, consequently giving erratic potentials, were discarded.

The arrangement of the electrodes was the following: For every measurement there were two reference electrodes, two alkali metal electrodes, and two alkali metal amalgam electrodes of identical composition. The cell, the electrode holders, and the cup electrode, besides all volumetric flasks and glassware, were cleaned prior to each experiment by concentrated nitric acid and were rinsed several times with distilled water. Periodically the cells were cleaned with concentrated sodium hydroxide, dilute sulfuric acid, and distilled water. Occasionally the cells and the cup electrodes were cleaned with an ultrasonic vibrator to remove solids from the glass. All glassware was dried in a vacuum oven at 50μ and 200°C for at least 24 hr and then transferred quickly into the glove box.

Assembly of cell.—The six-compartment cell was filled with approximately 100 cm³ solution of a specific concentration of the alkali metal chloride in $AlCl_3$ (1m)-PC. Thallium amalgam was dispensed into the cup of each of the two reference electrodes, a small amount of TlCl was spread on the surface, the ground joints were lubricated, and the reference electrodes were inserted into the cell. The alkali metal amalgam was then dispensed into the cups of each of the two-cup electrodes and was inserted into the cell. The alkali metal wire was cut, connected to the stainless steel holders, and inserted into the cell. The cell was then closed and removed from the glove box. The cell was next suspended in a constant temperature water bath for equilibrium and micropolarization measurements (3). The measurements were done at 25° and 35°C, ±0.01°C.

Cell potential measurements.—Measurements of the cell potentials were taken with a John Fluke Model 887—A differential voltmeter (accuracy ±0.005 mV) which was calibrated against an Eppley Laboratory, low temperature coefficient standard cell.

The measurements began 15 min after the suspension of the cell in the bath. Measurements included: (*i*) Cell potentials between the alkali metal electrodes and the reference electrodes. (*ii*) Cell potentials between the alkali metal amalgam electrodes and the reference electrodes. (*iii*) Potentials between the alkali metals and their amalgams. (*iv*) Bias potentials between the two alkali metal electrodes, the two alkali metal amalgam electrodes, and the two Tl(Hg)/TlCl reference electrodes. The potential measurements were repeated each 30 min for the first few hours and then were recorded several times each day for at least one week. The cell was then transferred to the 35°C bath and identical measurements were taken. The cell then was transferred back to the 25°C bath and the first series repeated.

Micropolarization measurements were conducted during the potential measurement period. The alkali metal electrodes were polarized in both cathodic and anodic directions and the reversibility of the electrodes was checked.

Results

Tables I-V contain the results of the experimental measurements of the general cell

$$M(s)/MCl(m),\ AlCl_3(1m)\ \text{in PC}/TlCl(s)/Tl(Hg)$$

at 25° and 35°C, where M represents Li, Na, K, Rb, and Cs. The measurements were repeated for each metal at different alkali metal chloride molalities. The concentration of the thallium amalgam, the same in all experiments, was 4.749% by weight.

The first column in each table gives the concentration of the alkali metal chloride in molality units (moles of MCl per 1000g of pure PC). The measured cell potential in volts is listed in the second column.

Table I. Results of cell potential measurements, lithium system

		25°C			35°C	
m	E	E_1	E_2	E	E_1	E_2
1.0	2.3571	2.2621	2.2621	2.3594	2.2614	2.2614
0.5	2.3848	2.2898	2.2542	2.3891	2.2911	2.2543
0.25	2.4044	2.3094	2.2382	2.4075	2.3095	2.2359
0.25	2.4179	2.3229	2.2517	2.4210	2.3230	2.2494
0.10	2.4160	2.3210	2.2027	2.4193	2.3213	2.1991
0.10	2.4090	2.3140	2.1957	2.4123	2.3153	2.1931
0.10	2.4199	2.3249	2.2066	2.4233	2.3253	2.2031
0.05	2.4371	2.3421	2.1882	2.4404	2.3424	2.1833
0.01	2.4601	2.3651	2.1255	2.4641	2.3661	2.1216
0.005	2.4707	2.3757	2.1035	2.4769	2.3789	2.0976
0.005	2.4740	2.3790	2.1068	2.4800	2.3820	2.1007
0.002	2.4591	2.3641	2.0449	2.4693	2.3713	2.0413

Table II. Results of cell potential measurements, sodium system

		25°C			35°C	
m	E	E_1	E_2	E	E_1	E_2
0.5	2.1790	2.0840	2.0484	2.1874	2.0894	2.0526
0.25	2.1875	2.0925	2.0213	2.1986	2.1006	2.0270
0.10	2.1863	2.0913	1.9730	2.2037	2.1057	1.9834
0.01	2.2440	2.1490	1.9124	2.2621	2.1641	1.9196
0.01	2.2446	2.1496	1.9130	2.2607	2.1627	1.9182

Table III. Results of cell potential measurements, potassium system

		25°C			35°C	
m	E	E_1	E_2	E	E_1	E_2
1.0	2.404	2.309	2.309	2.422	2.324	2.324
1.0	2.413	2.318	2.318	2.430	2.332	2.332
0.5	2.436	2.341	2.306	2.452	2.354	2.317
0.5	2.433	2.338	2.303	2.449	2.351	2.314
0.25	2.473	2.378	2.306	2.516	2.418	2.344
0.25	2.468	2.373	2.302	2.511	2.413	2.340
0.1	2.507	2.412	2.294	2.526	2.428	2.306
0.01	2.511	2.416	2.179	2.536	2.438	2.193
0.0025	2.551	2.456	2.148	2.572	2.474	2.156

Table IV. Results of cell potential measurements, rubidium system

m	25°C E	 E_1	 E_2	35°C E	 E_1	 E_2
1.0	2.353	2.258	2.258	2.354	2.256	2.256
0.5	2.452	2.357	2.321	—	—	—
0.25	2.487	2.392	2.320	—	—	—
0.10	2.479	2.384	2.266	2.489	2.391	2.269
0.10	2.476	2.381	2.263	2.487	2.389	2.267
0.05	2.475	2.380	2.226	2.491	2.394	2.234
0.01	2.497	2.402	2.165	2.524	2.426	2.181
0.0025	2.540	2.445	2.137	2.595	2.497	2.179

Table V. Results of cell potential measurements, cesium system

m	25°C E	 E_1	 E_2	35°C E	 E_1	 E_2
1.0	2.403	2.308	2.308	2.416	2.318	2.318
1.0	2.403	2.308	2.308	2.414	2.316	2.316
1.0	2.397	2.302	2.302	2.412	2.314	2.314
0.5	2.475	2.380	2.345	2.496	2.398	2.361
0.25	2.508	2.413	2.342	2.539	2.441	2.368
0.10	2.490	2.395	2.277	2.526	2.428	2.305
0.10	2.505	2.410	2.291	2.537	2.439	2.316
0.01	2.515	2.420	2.183	2.556	2.458	2.213
0.01	2.510	2.415	2.178	2.551	2.453	2.209
0.0025	2.555	2.460	2.152	2.606	2.508	2.189
0.0010	2.529	2.435	2.080	2.581	2.483	2.116

This value for each concentration is the average value of the potential of the two alkali metal electrodes *vs.* the two reference electrodes. The potential difference between two thallium amalgam-thallous chloride reference electrodes was always smaller than 1 mV. The bias potential between the two alkali metal electrodes was different for the various metals. The bias potential was smaller than 1, 1, 10, 5, 5 mV for the Li, Na, K, Rb, and Cs systems, respectively.

The potential E_1 is tabulated in the third column and represents the corrected value of E for the thallium amalgam concentration. The correction was taken from the work of Richards, and Daniels (16), who measured the potentials between different thallium amalgam concentrations and pure thallium.

The function E_2 is listed in the fourth column and the method used to obtain this function is given below. The potential of the cell

$$\mathrm{M(s)/MCl}(m),\ \mathrm{AlCl_3(1m)\ in\ PC/TlCl(s)/Tl(s)}$$

is given by

$$E_1 = E^\circ{}_1 - RT/\mathbf{F}\ln(m_{\mathrm{Cl}^-}m_{\mathrm{M}^+}\gamma_{\mathrm{Cl}^-}\gamma_{\mathrm{M}^+}) \qquad [1]$$

where m is the molality and γ the activity coefficient of a particular ion. Since the molality of $AlCl_3$ is held constant, it is convenient to choose the reference state as $AlCl_3$(1m) in PC. By this convention, the solvent is considered to be a unit molality solution of $AlCl_3$ in PC and not pure PC as usual. The cell potential according to this convention is given by

$$E_1 = E^\circ{}_2 - 2RT/\mathbf{F}\ln(m_{\mathrm{MCl}}\gamma_{\mathrm{MCl}}) \qquad [2]$$

where $E^\circ{}_2$ is the standard oxidation potential of the cell in $AlCl_3$(1m)-PC solution. The standard state of the solute is taken at infinite dilution of the alkali metal chloride in $AlCl_3$(1m)-PC solution where the activity coefficient of the alkali metal chloride approaches unity. The problem of determining $E^\circ{}_2$ and thus the activity coefficients at different concentrations of MCl involves extrapolation to infinite dilution. The method of extrapolation to infinite dilution using the Guggenheim equation (8) cannot be employed here since the ionic strength is very high. Instead, rearranging Eq. [2] gives

$$E_2 = (E_1 + 2RT/\mathbf{F}\ln m_{\mathrm{MCl}}) = E^\circ{}_2 - 2RT/\mathbf{F}\ln\gamma_{\mathrm{MCl}} \qquad [3]$$

Following the method presented by Lewis, Randall, Pitzer, and Brewer (17) (pp. 315-316), if we plot the left-hand side of Eq. [3] as ordinate against some function of m_{MCl} as abscissa, the limit approached by the ordinate at infinite dilution is equal to $E^\circ{}_2$. It is common to extrapolate with $(m_{\mathrm{MCl}})^{1/2}$ as abscissa since such a choice should give a curve approximating linearity at high dilution following the Debye-Hückel limiting law. However, here this dependence is used to expand the low concentration range. Figures 2 and 3 show the plot of E_2 *vs.* $(m_{\mathrm{MCl}})^{1/2}$ for all the alkali metals at 25° and 35°C, respectively. The intercepts at zero molalities give $E^\circ{}_2$, the standard potentials at $AlCl_3$(1m)-PC solution. The difference between the extrapolated values at 25° and 35°C gives the temperature dependence of the standard potential at constant pressure. The results of the extrapolations are given in Table VI.

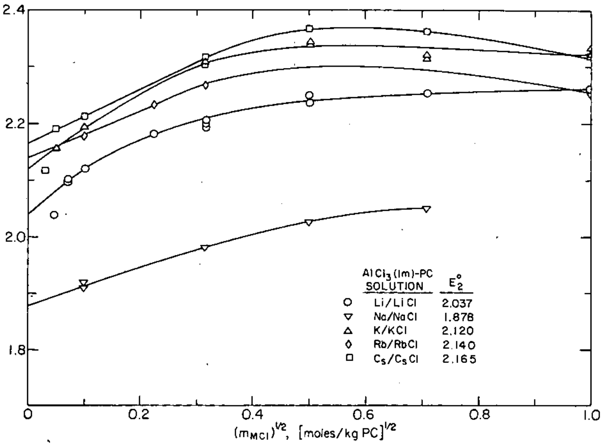

Fig. 2. EMF measurements of the cell: M/MCl(m), $AlCl_3$(1m)-PC/TlCl(s), Tl(s) at 25°C.

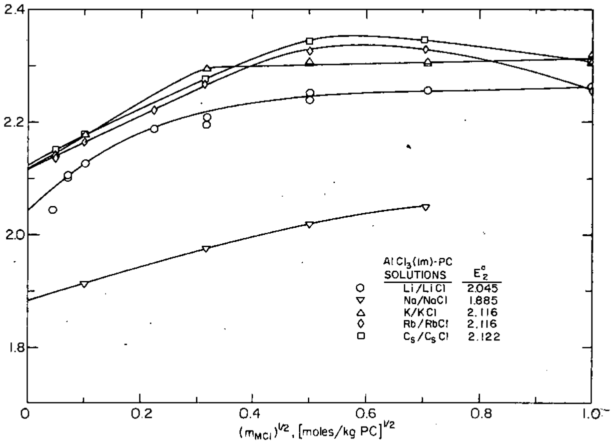

Fig. 3. EMF measurements of the cell: M/MCl(m), $AlCl_3$(1m)-PC/TlCl(s), Tl(s) at 35°C.

From the standard cell potentials and their variation with temperature, the standard free energy $\Delta G^\circ{}_2$, entropy $\Delta S^\circ{}_2$, and enthalpy $\Delta H^\circ{}_2$ can be calculated

$$\Delta G^\circ{}_2 = -n\mathbf{F}E^\circ{}_2 \qquad [4]$$

$$\Delta S^\circ{}_2 = n\mathbf{F}(\partial E^\circ{}_2/\partial T)_p \qquad [5]$$

$$\Delta H^\circ{}_2 = -n\mathbf{F}(E^\circ{}_2 - T(\partial E^\circ{}_2/\partial T)_p) \qquad [6]$$

These functions are related to the following cell reaction

Table VI. Standard cell potentials at 25° and 35°C

Metal	$E^\circ{}_2$, 25°C	$E^\circ{}_2$, 35°C	$(\partial E^\circ{}_2/\partial T)_p$
Li	2.045 ± 0.010	2.037 ± 0.010	−0.8 10^{-3}
Na	1.885 ± 0.010	1.878 ± 0.010	−0.7 10^{-3}
K	2.116 ± 0.020	2.120 ± 0.020	+0.4 10^{-3}
Rb	2.116 ± 0.020	2.140 ± 0.020	+2.4 10^{-3}
Cs	2.122 ± 0.020	2.165 ± 0.020	+4.3 10^{-3}

Table VII. Standard free energies, entropies, and enthalpies for reaction [7] for all the alkali metals

Metal	$\Delta G°_2$, kcal/mol 25°C	$\Delta G°_2$, kcal/mol 35°C	$\Delta S°_2$, e.u. 25°C	$\Delta H°_2$, kcal/mol 25°C	$\Delta H°_2$, kcal/mol 35°C
Li	−47.2	−47.0	−18.4	−52.7	−52.7
Na	−43.5	−43.3	−16.1	−48.3	−48.3
K	−48.8	−48.9	+9.2	−46.0	−46.1
Rb	−48.8	−49.3	+55.3	−32.3	−32.3
Cs	−48.9	−49.9	+64.7	−29.6	−29.6

$$\mathrm{M(s)\ TlCl(s) + 1\ mole\ AlCl_3 + 9.8\ mole\ PC \rightleftharpoons}$$

$$\mathrm{MCl\ (in\ AlCl_3(1m)\text{-}PC\ solution,}\ a_{\mathrm{MCl}} = 1) + \mathrm{Tl(s)} \quad [7]$$

Table VII presents $\Delta G°_2$, $\Delta S°_2$, and $\Delta H°_2$ on the molal scale for the above cell reaction at 25° and 35°C. The uncertainty in $\Delta S°_2$ and $\Delta H°_2$ is quite high because they were calculated from the difference between extrapolated values.

EMF of the alkali metal-alkali metal amalgam cells.—In addition, emf's of the cell M(s)/MCl(m), $AlCl_3$(1m),PC/M(Hg) were also measured. The concentrations of the Na, K, and Rb amalgams were adjusted to the exact concentrations of the amalgams used by Lewis and his co-workers (18-21). This was done in order to be able to make comparison with emf data for the single amalgam concentrations listed in the literature. In the case of lithium amalgam, the activity coefficient data of lithium was obtained from the work of Cogley and Butler (22). The cesium amalgam concentration did not match the concentration used by Bent *et al.* (23). The agreement between the present measurements and those in the literature is in all cases better than 4.2 mV.

Activity coefficients of the alkali metal chlorides in $AlCl_3(1m)$-PC solution.—Mean molal activity coefficients of the alkali metal chlorides in $AlCl_3$(1m) solution in PC were calculated from

$$\ln \gamma_{\mathrm{MCl}}\ (\mathbf{F}/2RT)\ (E°_2 - E_2) - \ln m_{\mathrm{MCl}} \qquad [8]$$

where $E°_2$ is the extrapolated value of the standard cell potential given in Table VI. The calculated activity coefficients at 25°C are given in Table VIII. Figure 4 presents the plots of ln γ_{MCl} *vs.* $(m_{\mathrm{MCl}})^{1/2}$ for all the alkali metal chlorides. It should be mentioned again that the reference state is $AlCl_3$(1m) in PC and not the pure solvent.

Discussion

EMF measurements of the cell without transference: M(s)/MCl(m), $AlCl_3$(1m)-PC/TlCl(s)/Tl(Hg) gave reproducible results. Potential measurements involving the lithium and sodium systems were especially reproducible. The greatest scattering of data points was experienced with the potassium system. Potassium electrodes were less stable in PC and in some cases turned purple after a few days of repeated measurements. This was probably due to the high sensitivity of K electrodes to small traces of water. Lithium and sodium gave reproducible results within ± 1 mV, while rubidium and cesium were somewhat less reproducible, and their bias potentials varied within ± 5 mV, probably because of difficulties experienced in preparing the electrodes in the molten state.

Table VIII. Activity coefficients of the alkali metal chlorides in $AlCl_3$ (1m)-PC solution at 25°C

			$-\ln \gamma_{\mathrm{MCl}}$		
m	LiCl	NaCl	KCl	RbCl	CsCl
1.0	4.051		3.808	2.768	3.738
0.5	3.892	3.181	3.623	3.990	4.455
0.25	3.719	2.652	3.626	3.970	4.398
0.10	2.863	1.713	3.423	2.885	3.273
0.05	2.604			2.143	
0.01	1.427	0.442	1.193	0.961	1.263
0.005	0.962				
0.0025	0.989		0.631	0.412	0.872

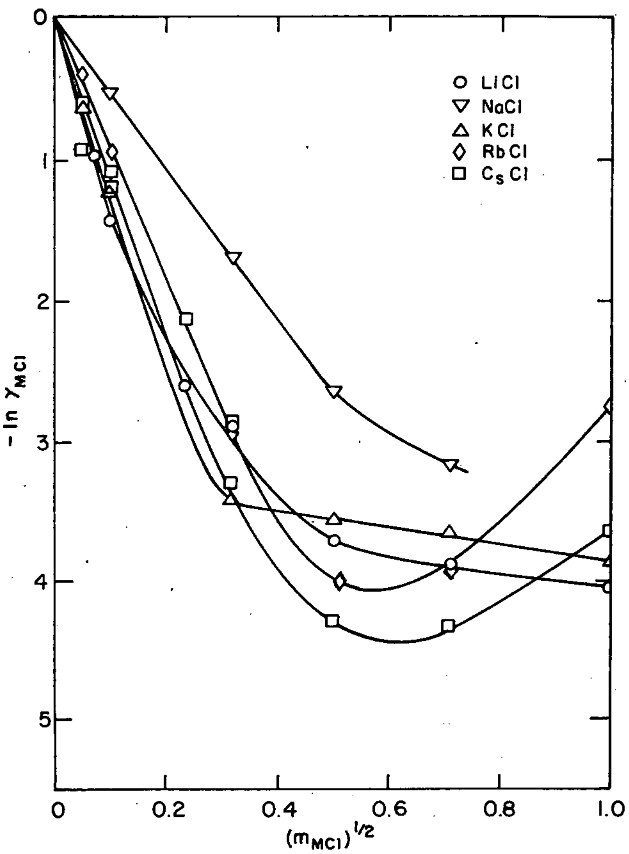

Fig. 4. Activity coefficients of the alkali metal chlorides in $AlCl_3$(1m)-PC solution at 25°C.

The change in cell potential with time was followed by measuring the potentials every 30 min for the first few hours. The potentials were measured then for at least one week before the cell was disassembled. For the first half-hour, especially for solutions having a low concentration of alkali metal chloride, changes in potentials were observed. The potential was then steady within ±5 mV for a few hours, followed by a steady decrease in the cell potential, during the next day. In every case the potential drifted toward the discharge of the cell. The decrease in potential was faster for low alkali metal chloride concentrations, and was minimal when the molality of MCl approached unity or 1:1 ratio with respect to $AlCl_3$ molality in PC. Figure 5 presents the time dependence of the potential for two lithium cells. The lower curve represents the change in potential of a cell containing LiCl (1.0m) in $AlCl_3$(1m)-PC. The upper curve shows the behavior of a cell containing LiCl (0.01m) in $AlCl_3$(1m)-PC.

Similar behavior of cell discharge was observed by Salomon (5) for the alkali metal halides in PC. A steady decrease in cell potentials was observed for lithium halides in DMSO (24, 25), dimethylformamide (12), and N-methylformamide (26). A strong decrease of cell potential with time was observed in the cell Pt, H_2/HCl(m)/AgCl, Ag in formamide (27-29); the true cell potentials were obtained by extrapolating the observed potentials to zero time. Here a decrease of approximately 20 mV was observed during a period of 2 hr (27-29).

The reasons for the steady decrease in cell potentials have been attributed to either solubility and diffusion of the thallous halide and subsequent reaction with the alkali metal (24, 25), or the reaction of the alkali metal with the solvent or with solvent impurities such as water (5). Salomon attributed the phenomena to the reactivity of the alkali metals with impurities rather

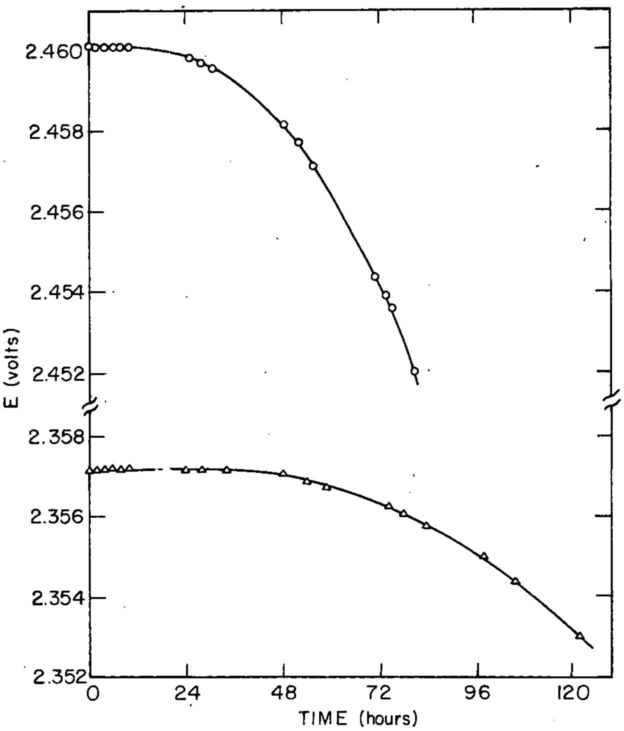

Fig. 5. Time dependence of lithium cell potential at 25°C. ○, $m_{LiCl} = 1.0$ and △, $m_{LiCl} = 0.01$.

than to TlCl diffusion across the cell, because the solubility of TlCl in pure PC is extremely low ($K_{sp} = 10^{-12.4}$). In addition, fritted glass was used to slow the diffusion of the thallium species across the cell. However in the present work TlCl is probably somewhat more soluble in the presence of an excess of $AlCl_3$. The behavior of the cell potentials in the present work was similar to the one reported by Smyrl and Tobias for LiCl in DMSO (13), where, after a period of several hours of relatively constant potential, the potential started to decrease steadily due to the reaction

$$Li(s) + TlCl(solution) \rightarrow Tl(s) + LiCl(solution)$$

The standard cell potentials of the alkali metals in $AlCl_3$(1m)-PC solution, relative to Tl/TlCl, are presented in Table VI along with the cell potential temperature coefficients. These results were obtained by extrapolation to infinite dilution with respect to the alkali metal chloride molalities. The order of the standard potentials in the alkali metal series does not follow that in aqueous solution, where lithium has the highest standard potential. The standard potentials of the alkali metals in water and in several other solvents are presented in Table IX, along with the present results. The present results, as well as Salomon's data assign a noticeably higher standard potential to potassium than to lithium. Since the work of Salomon does not include measurements of the rubidium and cesium cells, further comparison cannot be made. Cesium, followed by rubidium shows the highest oxidation potentials in $AlCl_3$(1m)-PC. This is not the case in acetonitrile, N-MF, and water, where lithium has the highest oxidation potential (see Table IX). It may be proper to quote the prediction made by Lewis and Argo in 1915 (21) concerning the peculiarity of the order of the standard potentials in the alkali metal series: "The potentials of the alkali metals follow a curious order, namely, lithium, rubidium, potassium, and sodium. It is interesting, however, to observe that this is the order of the heats of formation of the several ions in aqueous solution. In order to illustrate this fact, the heat of formation of the chlorides of the four metals in aqueous solution are: 102, 101, 101, 96 kcal/mole for LiCl, RbCl, KCl, and NaCl, respectively. The heat of formation of aqueous cesium chloride is given as 105 kcal/mole, and if this figure is correct, we might predict the potential of cesium to be higher than any of the other alkali metals" (21). However, this prediction did not materialize when 14 years later Bent, Forbes, and Forziani (23) obtained the normal electrode potential of cesium, $E° = 2.923$ volts, "...very close to the corresponding value for rubidium, but still 34 millivolts below that for lithium."

Figures 2 and 3 present the potential measurements and the extrapolation to infinite dilution. The fact that almost linear behavior is obtained by plotting the potential E_2 *vs.* $(m_{MCl})^{1/2}$ is very helpful in obtaining the standard potentials, although it should be remembered that this behavior is not well described by the Debye-Hückel limiting law, because the reference solvent was a solution of $AlCl_3$ in PC, in which the ionic strength is very high. The plotting of the results *vs.* the square root of the molality was adopted to expand the dilute region and to obtain a better accuracy in the extrapolation.

The extrapolation procedure of the emf measurements does not involve any assumption concerning the nature of the complexes and ionic species in solution. The predominant ions in a solution of MCl in $AlCl_3$-PC solution are M^+, $Al(PC)_n{}^{3+}$, and $AlCl_4{}^-$. Keller *et al.* (30) studied directly the ionic equilibria of $AlCl_3$ in PC using NMR technique. From the ^{27}Al spectra it was concluded that the main species are $Al(PC)_n{}^{3+}$ and $AlCl_4{}^-$, similar to the species present in acetonitrile. High resolution ^1H spectra of 1M $AlCl_3$ in PC indicates peaks due to coordinated PC as well as bulk PC. From the ^1H and the ^{27}Al spectra, Keller *et al.* (30) showed that the Al^{3+} coordination number (n) is six. Therefore the dissociation of $AlCl_3$ in PC proceeds according to

$$AlCl_3 + 6/4\,PC \rightarrow 1/4\,Al(PC)_6{}^{3+} + 3/4\,AlCl_4{}^- \quad [9]$$

Furthermore it was observed that the addition of LiCl to an $AlCl_3$-PC solution reduces the concentration of the coordinated Al species, and at the saturation point where the LiCl:$AlCl_3$ ratio is 1:1 the coordinated Al species disappears. Such observation can be explained by the reaction between LiCl and $Al(PC)_6{}^{3+}$ to give mainly $AlCl_4{}^-$

Table IX. Standard oxidation potentials in nonaqueous solvents

	Acetonitrile	N-MF	Formamide	Ethylene glycol	Propylene carbonate			PC-$AlCl_3$(1m)	H_2O
Li	3.23	3.124	—	2.996	1.85080*	1.84223*	1.8452	2.045	3.045
Na	2.87	2.807	—	2.686	—	—	1.6188	1.885	2.714
K	3.16	3.021	2.872	2.897	—	—	1.934	2.116	2.925
Rb	3.17	—	2.855	—	—	—	—	2.116	2.925
Cs	3.16	2.987	—	—	—	—	—	2.122	2.923
Ref. elec.	H_2/H^+	Ag/AgCl	H_2/H^+	Ag/AgBr	Tl/TlCl	Tl/TlBr	Tl/TlI	Tl/TlCl	H_2/H^+
Reference	(33, 34)	(35)	(36)	(38)	(5)	(5)	(6, 7)	(present work)	(37)

* Salomon made an error in the thallium amalgam corrections in his work with LiCl and LiBr in PC. The corrections at 25°C for thallium amalgam compositions of 3.147 and 7.76% wt are 112.5 and 78.6 mV, respectively, as is evident from the work of Richards and Daniels (16), and not 135.34 and 94.6 mV as reported by Salomon (5). The results obtained for the other systems studied by Salomon cannot be checked, as detailed data are not available (6, 7).

$$x\text{LiCl} + \tfrac{1}{4}\text{Al(PC)}_6{}^{3+} + \tfrac{3}{4}\text{AlCl}_4{}^- \rightarrow x\text{Li}^+ + (1-x)/_4\text{Al(PC)}_6{}^{3+} + (3+x)/_4\text{AlCl}_4{}^- + 3x/_2\text{PC} \quad [10]$$

At the saturation point where $x = 1$, all the coordinated $Al(PC)_6{}^{3+}$ converted to $AlCl_4{}^-$ and the predominant species present are Li^+ and $AlCl_4{}^-$. Keller *et al.* (30) summarizes the results for solutions of $AlCl_3$ in DMF, AN, and PC. The complexing strength of Al^{3+} toward Cl^- is stronger than toward PC, AN, and water, but weaker than toward DMF where the dominant species are $Al[DMF]_6{}^{3+}$ and Cl^-. Movius and Matwiyoff (31) report PMR data for aluminum halides (AlX_3) in DMF which can be interpreted in terms of second coordination sphere interaction between a well-defined $Al(DMF)_6{}^{3+}$ ion and X^-.

The potentials for lithium cells in which the molality of LiCl was less than 0.005m showed a substantial drift to lower values. This can be observed in Fig. 2 and 3 by the tailing off at the very low LiCl concentration. The potential at 0.002m LiCl was not included in the extrapolation. Tailing off at low concentration was observed by others, especially for lithium cells in DMSO (13, 24), N-methyl formamide (26), and in dimethyl formamide (12). Deviations were not observed in LiI solution in PC (7), nor in LiI solution in DMSO (32). Deviations were not observed in sodium and potassium cells in PC (6, 7), nor in sodium, potassium, and rubidium cells in N-methyl formamide (26).

The standard potentials in the present work are given on a molal basis. The molal basis has been chosen because the molecular weight of PC is more than 5 times larger than that of water. Since many authors present their results on a molar basis, it should be remembered that the standard potential, on a molal basis, can be converted into a molar basis, according to the following relation

$$E^\circ{}_c = E^\circ{}_m + \frac{2RT}{\mathbf{F}} \ln \rho_0 \quad [11]$$

where $E^\circ{}_c$ and $E^\circ{}_m$ are the standard potentials on a molar and molal basis, respectively, and ρ_0 is the density of the solvent. The solvent in the present case is an $AlCl_3$(1m)-PC solution, and its density is reported as 1.2628 and 1.2530 g/cm³ at 25° and 35°C, respectively (1). The standard potentials of the alkali metals, on a molar basis are presented in Table X. In addition, the standard potentials on a mole fraction basis are presented as well. The mole fraction basis is probably the most suitable way to present thermodynamic data, where the solute mole fraction is comparable with the solvent mole fraction. The standard potential on a mole fraction basis can be obtained from the following equation

$$E^\circ{}_N = E^\circ{}_m + \frac{2RT}{\mathbf{F}} \ln \left(\frac{1000}{\text{M.W.}} + 1 \right) \quad [12]$$

where $E^\circ{}_N$ is the standard potential on a mole fraction basis, and M.W. is the molecular weight of the solvent. In the present case, the reference state is a 1m solution of $AlCl_3$ in PC.

The behavior of the sodium curves in Fig. 2 and 3 is different from the rest of the alkali metals. The solubility of NaCl in $AlCl_3$(1m)-PC solution was around 0.5m, in contrast to the rest of the alkali metal chlorides, which dissolved corresponding to a 1:1 ratio with respect to $AlCl_3$. There is no explanation for this unexpected behavior, although there are indications that the solubilitites of RbCl and CsCl in $AlCl_3$(1m)-PC are not exactly 1.0m but drop slightly upon standing. The decrease in the potentials at high concentrations for the rubidium and cesium systems, given in Fig. 2, indicates probable solvate formation.

Table X. Standard oxidation potentials on a molar and a mole fraction basis for $AlCl_3$ (1m)-PC cells

	$E^\circ{}_{2,c}$ 25°C	$E^\circ{}_{2,c}$ 35°C	$E^\circ{}_{2,N}$ 25°C	$E^\circ{}_{2,N}$ 35°C
Li	2.054	2.046	2.162	2.158
Na	1.894	1.887	2.002	1.998
K	2.125	2.127	2.233	2.241
Rb	2.125	2.149	2.116	2.261
Cs	2.131	2.174	2.239	2.286

The activity coefficients of the alkali metal chlorides in $AlCl_3$-PC solution are shown in Fig. 4. The sharp decrease in the activity coefficients at low concentrations is due to the reaction between the chloride ions and Al^{3+} species yielding $AlCl_4{}^-$. Since $AlCl_3$ is part of the solvent, this decrease in the activity coefficients is equivalent to systems where the solute reacts with the solvent, *e.g.*, NH_3 in water or hydrate formation in aqueous solution.

Estimation of the standard potentials of the alkali metals in pure PC.—The standard potentials obtained were calculated with respect to the cell M(s)/MCl, $AlCl_3$(1m)-PC/TlCl(s), Tl(s) where the standard state was chosen as infinite dilution of MCl in $AlCl_3$(1m)-PC solution. The standard potentials of the alkali metals in pure PC can be measured from the cell M(s)/MCl, PC/TlCl(s), Tl(s). However, the solubilities of the alkali metal chlorides in PC are very low, and only LiCl is soluble enough to permit accurate potential measurements. Salomon measured the standard potential of lithium in LiCl solution in PC; however, in order to establish a scale of standard potentials in PC for the rest of the alkali metals, he switched to the alkali metal iodides which are soluble in PC. Salomon did not measure the standard potentials of rubidium and cesium.

An estimation of the standard potentials of cells of the alkali metal chlorides in pure PC can be made on the basis of the results of the present work and the standard potential of the LiCl cell as reported by Salomon (5). The standarad potential of the cell Li(s)/LiCl(m), $AlCl_3$(1m),PC/TlCl(s), Tl(s) is given by

$$E_1 = E^\circ{}_1 - \frac{RT}{\mathbf{F}} \ln \left(m_{Li^+}\gamma_{Li^+}m_{Cl^-}\gamma_{Cl^-}\right) \quad [13]$$

where $E^\circ{}_1$ is the standard potential at infinite dilution. The cell potential on the basis of $AlCl_3$(1m)-PC as a reference state is given by

$$E_1 = E^\circ{}_2 - \frac{2RT}{\mathbf{F}} \ln \left(m_{LiCl}\gamma_{LiCl}\right) \quad [14]$$

As $m_{LiCl} \rightarrow 0$

$$E^\circ{}_2 - E^\circ{}_1 = -\frac{RT}{\mathbf{F}} \ln \left(m_{Li^+}\gamma_{Li^+}m_{Cl^-}\gamma_{Cl^-}\right) \quad [15]$$

The left-hand side of Eq. [13] can be calculated, since $E^\circ{}_2$ was measured in the present work, and $E^\circ{}_1$ for lithium is reported by Salomon as, $E^\circ{}_1 = 1.85080V$. (This value is the corrected one, since Salomon made an error in the thallium amalgam correction, see Table IX)

$$-\frac{RT}{\mathbf{F}} \ln \left(m_{Li} + \gamma_{Li} + m_{Cl^-}\gamma_{Cl^-}\right)_{m_{LiCl\rightarrow 0}} = 2.045 - 1.851 = 0.194V$$

If we assume that this value does not change much going through the alkali metal series, we can estimate the standard potentials $E^\circ{}_1$ for the rest of the alkali metals

$$E^\circ{}_1 = E^\circ{}_2 - 0.194$$

Table XI summarizes the approximated standard potentials of the cell M(s)/MCl, PC/TlCl(s), Tl(s).

On the basis of these estimated standard oxidation potentials, it is expected that even in pure PC the standard oxidation potential of Cs will be the highest, followed by Rb, K, Li and Na.

Table XI. Estimated standard oxidation potentials for the alkali metals in pure PC

Cell	E°_1, volt	ΔG°_1, kcal/mole
Li/LiCl,PC/TlCl,Tl	1.85080*	−42.9*
Na/NaCl,PC/TlCl,Tl	1.691	−39.0
K/KCl,PC/TlCl,Tl	1.922	−44.3
Rb/RbCl,PC/TlCl,Tl	1.922	−44.3
Cs/CsCl,PC/TlCl,Tl	1.928	−44.5

* Measured by Salomon (5).

Ionic equilibria considerations.—The predominant ions in a solution of MCl in $AlCl_3$-PC solution are M^+, $Al(PC)_6{}^{3+}$, and $AlCl_4{}^-$. A rough calculation was made of the equilibrium constant of the reaction

$$AlCl_4{}^- \overset{K_4}{\rightleftarrows} Al^{3+} + 4Cl^- \qquad [16]$$

on the assumption that this equilibrium accounts for all the difference between the activity of MCl and that of a typical univalent salt. The calculations were performed only in the case of LiCl because its standard potential on the pure solvent basis was obtained by Salomon (5)

The fourth ionization constant K_4 is given by

$$K_4 = \frac{(Al^{3+})(Cl^-)^4}{(AlCl_4{}^-)} \qquad [17]$$

Multiplying and dividing by (Li^+) results in

$$K_4 = \frac{\gamma^4{}_{3\text{-}1}[Al^{3+}][Cl^-]^3 a_{LiCl}}{\gamma^2{}_{1\text{-}1}[AlCl_4{}^-][Li^+]} \qquad [18]$$

where brackets indicate molality and parentheses activity.

For a constant ionic strength we can define a new constant

$$K_4' = \frac{\gamma^2{}_{1\text{-}1}}{\gamma^4{}_{3\text{-}1}} K_4 = \frac{(1-m)a_{LiCl}}{(3+m)m}[Cl^-]^3 \qquad [19]$$

where m is the molality of the added LiCl. The activity of LiCl based on pure PC as a standard state, a_{LiCl}, can be estimated from the present emf measurements and the standard potential $E^\circ = 1.8508V$ obtained by Salomon (5) for the cell: Li/LiCl in PC/TlCl/Tl

$$E = 1.8508 - (RT/\mathbf{F}) \ln a_{LiCl} \qquad [20]$$

The ionic strength is fairly constant over most of the experimental range and can be evaluated for the general case of adding m moles of LiCl to 1m solution of $AlCl_3$ in PC (see Eq. [10]) according to

$$I = \frac{1}{2}\sum_i m_i z_i{}^2 = \frac{1}{2}\left[\frac{(3+m)}{4}(-1)^2 + \frac{(1-m)}{4}(+3)^2 + m(+1)^2\right] = \frac{(12-4m)}{8} \qquad [21]$$

When $m = 0$ the ionic strength is $I = 1.5$ and drops to $I = 1.0$ when $m = 1.0$. The ionic strength is fairly constant up to $m = 0.25$ and over this range we can assume the ratio $\gamma^2{}_{1\text{-}1}/\gamma^4{}_{3\text{-}1}$ is fairly constant.

Table XII presents the calculations of $K_4'/[Cl^-]^3$ as a function of the added molality of LiCl, m, and the total ionic strength, I. As can be seen from Table XII the chloride concentration $[Cl^-]$ increases very slightly as we add LiCl. Although we increase the LiCl concentration up to 50 times, the free chloride concentration increases by a factor of merely 1.8. Also, it should be kept in mind that K_4' depends on the ionic strength since it includes the ratio of the activity coefficients. However, as has been mentioned earlier, the ionic strength remains fairly constant up to 0.25m of added LiCl.

Table XII. Instability constant K'_4 and free chloride molality

m	$10^9 \times a_{LiCl}$	$I^{1/2}$	$10^8 \times (K'_4/[Cl^-]^3)$	$[Cl]^-$
0.005	1.1	1.223	7.29	239.4 × $(K'_4)^{1/3}$
0.01	1.8	1.222	5.92	256.6
0.05	4.6	1.219	2.87	326.6
0.10	11.1	1.204	3.22	314.3
0.25	13.1	1.173	1.21	435.6
0.50	17.8	1.118	1.02	461.1
1.00	105.3	1.000	—	—

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